A theory for magnetic-field effects of nonmagnetic organic semiconducting materials

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A universal mechanism for strong magnetic-field effects of nonmagnetic organic semiconductors is presented. A weak magnetic field (less than hundreds mT) can substantially change the charge carrier hopping coefficient between two neighboring organic molecules when the two hopping states are not too symmetric. Under the illumination of lights or under a high electric field, the change of hopping coefficients leads also to the change of polaron density so that photocurrent, photoluminescence, electroluminescence, magnetoresistance and electrical-injection current become sensitive to a weak magnetic field. The present theory can not only explain all observed features, but also provide a solid theoretical basis for the widely used empirical fitting formulas.

One of the long-term[1–4] unsolved fundamental issues in organic physics is the mechanism behind the strong responses of electrical and optical properties of nonmagnetic organic semiconductors to a weak magnetic field, known as organic magnetic-field effect (OMFE). The recent revival interest in OMFE of organic semiconductors is largely due to its importance in fundamental science and technology applications[4]. Firstly, there is a belief that the OMFE can be used as a powerful tool to probe microscopic processes of organic materials. Secondly, the OMFE can be used to develop new multifunctional organic devices[5]. Experiments showed that OMFE has following surprising yet universal features. 1) The OMFE appears in vast different organic semiconductors without any magnetic elements at room temperature although the possible energy level shifts due to the presence of a magnetic field are orders magnitude smaller than the thermal energy and other energy scales. 2) The electroluminescence, photocurrent, photoluminescence, and electrical-injection current are very sensitive to weak magnetic field with both positive and negative OMFE though positive OMFE (or negative magnetoresistance (MR) in the convention terminology) at very weak field is typically observed. 3) The OMFE can often be fitted by two empirical formulas: $[B/(B + B_0)]^2$ and $B^2/(B^2 + B_0^2)$[6], where B is the applied magnetic field. In the theoretical side, it is known[3, 4] that familiar MR mechanisms such as Lorentz force, conventional hopping MR, electron-electron interaction and weak localization are highly unlikely to be the cause behind the OMFE. The current belief in the community is that the OMFE is intimately tied to spin physics involving spin configuration, spin correlation, and spin flip[4]. However, there is no convincing arguments why an extremely small Zeeman energy can beat other much larger energy scales in controlling electron spin dynamics to generate this OMFE. Both extensive experimental and theoretical studies so far are suggesting that a novel explanation is needed. This new MR mechanism should explain not

only all OMFE features, but also why the similar effects do not often appear in the usual inorganic semiconductors. In this report, we present such a theory that does not explicitly rely on the electron spin degrees of freedom. It is showed that the OMFE originates from the substantial change of electron hopping coefficient in a magnetic field because of narrow bandwidth of organic semiconductors and asymmetry in organic molecules.

Organic semiconductors have a few distinct properties that their inorganic counterparts do not have. Firstly, unlike an atom that is sphere-like, an organic molecule is highly irregular. As a result, organic molecular wavefunction has no obvious symmetry. Secondly, organic molecules in organic semiconductors are bonded by the Van der Waals force so that their bands are very narrow in comparison with an order of 10eV bandwidth for their inorganic counterparts [11]. Thirdly, the intramolecular excitons have strong binding energies of order of eV[4]. On the other hand, the electron and hole become polaron pair when they are located on different molecules because of weak intermolecular exciton binding energy[4]. The electrical properties of an organic semiconductor are mainly determined by the motion of polarons since the motion of excitons does not contribute to the electric current. The singlet excitons are responsible to the luminescence. A weak field should not change much of energy levels of various excitation states so that their populations at thermal equilibrium are not sensitive to a magnetic field because they depend only on the energy level distribution and the temperature. Any significant change in magnetoresistance near the quasiequilibrium state must come from the mobility change. The question is whether a weak field of 100mT can change the mobility of polarons in organic semiconductors. In the usual inorganic crystals with s-like wavefunction, the answer is no. However, we argue below that this can indeed happen in organic conjugated materials with highly irregular molecular wavefunction.
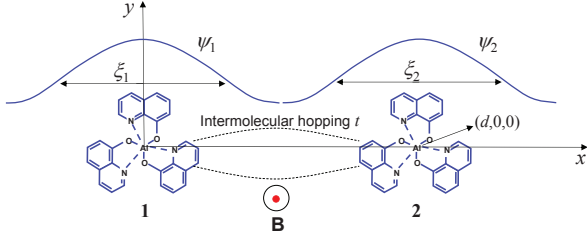
In order to understand why a weak magnetic field can

FIG. 1: Schematical draw of two organic molecules (Alq$_3$) separated by a distance d and aligned along x-direction. Molecule **1** is centered at the origin, and molecule **2** is centered at $(d,0,0)$. The field is assumed to be along z-direction. ψ_1 and ψ_2 are two localized states with localization lengths ξ_1 and ξ_2 on molecules **1** and **2**, respectively.

change charge carrier (electron and hole or polaron) mobility in an organic conjugated material, we consider a system with two molecules separated by a distance d as schematically shown in Fig. 1. One-electron Hamiltonian in a magnetic field can in general be described by

$$H = -\frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A})^2 + V_1 + V_2 \qquad (1)$$

where V_1 and V_2 are the potential created by molecules **1** and **2**, respectively. $\vec{A}$ is the vector potential due to magnetic field $\vec{B}$. For the simplicity and clarity, we shall assume that the two molecules are aligned along x-direction, the field is along the z-direction (pointing out of the paper). The important quantity for electron transport is the tunneling matrix element between two molecules. When an electron tunnels from an initially occupied state, say ψ_1 of molecule **1**, to empty state ψ_2 of molecule **2** with tunneling matrix t , it will contribute to the hopping probability P (per unit time), proportional to $|t|^2 \exp(-\Delta\epsilon_{12}/(KT))$, where $\Delta\epsilon_{12}$ describes the relative energy level with respect to the Fermi level[12]. The hopping conduction can be regarded as an electron diffusion process with a diffusion constant $D = Pd^2$, where d is the average distance between two neighboring molecules. According to the Einstein relation, the electron mobility μ is given by $\mu = eD/(KT)$ which is related to the conductivity in the conventional way[12]. Therefore, we can concentrate on how the tunneling matrix element depends on the magnetic field in order to study the magnetoresistance of the system.

In the tight-binding approximation[13], one of the authors in an early publication[14] has generalized the Bardeen's transfer matrix formalism to high dimension and in the presence of a magnetic field. In 3D, it is

$$t = \frac{\hbar^2}{m}\int[(\psi_1^\star\frac{\partial\psi_2}{\partial x} - \psi_2\frac{\partial\psi_1^\star}{\partial x}) - \frac{2i}{\phi_0}(\vec{A}\cdot\hat{x})\psi_1^\star\psi_2]|_{x=\frac{d}{2}}\,dydz, \qquad (2)$$

where $\phi_0 = c\hbar/e$ is the flux quanta. For small $\vec{A}$ when the magnetic length $l_B = \sqrt{\phi_0/B}$ is bigger than d, magnetic confinement that is responsible for the exponential

increase of resistance in the usual hopping conduction can be neglected and ψ_1 and ψ_2 do not depend on B to the zero order approximation. Then the magnitude of the field-independent part of t is order of

$$\frac{\hbar^2}{m\xi}\int\psi_1^\star\psi_2|_{x=\frac{d}{2}}\,dydz$$

while that of the field dependent part is

$$\frac{\hbar^2}{m}\frac{1}{l_B^2}\int y\psi_1^\star\psi_2|_{x=\frac{d}{2}}\,dydz.$$

$\xi^{-1} = \xi_2^{-1} + \xi_1^{-1}$, and ξ_1 and ξ_2 are the localization lengths of ψ_1 and ψ_2, respectively. Both terms depend on the nature of the wavefunctions. This explains why the OMFE value varys from sample to sample, and from material to material[4]. The second term vanishes for s-like wavefunction. This is why the similar phenomena do not show up in usual inorganic semiconductors. Due to the irregular structures of organic molecules, one will expect an appreciable value for the second term, resulting in a sizable change of the hopping probability.

Due to the Van der Waals bonding, the OMFE is measurable only under an optical injection of carriers or an electric carrier injection by an electric field above a threshold. When an organic semiconductor is under the illumination of a light or under a high electric field, the field dependent t results in a field dependence of polaron density. Take optical injection of carriers as an example, under the illumination of a light, an electron in a highest occupied molecular orbit (HOMO) absorbs a photon and jumps to a higher empty molecular orbit of the same molecule. As schematically illustrated in Fig. 2, the excited electron can either dump its excessive kinetic energy to its environment and forms an exciton with the hole left behind or jumps to neighboring molecules and becomes polarons. Depending on the relative probabilities of excited electrons (holes) staying in the same molecules and jumping to different molecules, the polaron density shall vary with the illumination intensity. Let us denote the probability (per unit time) of a pair of electron and hole on the same molecule forming an exciton by $P_0 \sim \hbar/\tau$, where τ is the typical time for a pair of electron and hole to form an exciton. P_0 is not sensitive to a weak field since the field cannot change much molecule orbits that determine P_0. Then the polaron generation rate per unit volume is $JP/(P_0 + P)$ where J is the photon absorption rate per unit volume and $P \propto |t|^2$ is the intermolecular hopping probability. Without the illumination of a light, polaron density shall reach its equilibrium density n_0 at a rate of $\gamma(n - n_0)$, where γ is polaron decay rate. At balance, $JP/(P_0 + P) = \gamma(n - n_0)$, thus the photon-generated polaron density n should be $n_0 + JP/[\gamma(P_0 + P)]$. Clearly, B-dependence of P results in a B−dependence of polaron density.

Since the OMFE can often be fitted by two empirical functions $B^2/(B^2 + B_0^2)$ and $[B/(B + B_0)]^2$[6], a correct
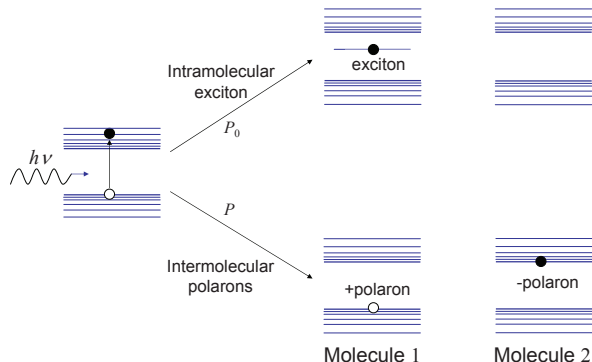
FIG. 2: Schematic illustration of polaron and exciton formation after a pair of electron and hole is created by a photon absorption. The excited electron-hole pair has probability P jumping to the neighboring molecules to form positive-charged and negative-charged polarons, and probability P_0 to form an exciton.

theory should be able to provide a theortical basis for the fact. According to Eq. (2), t takes a form of $B_0 + iaB$ with B_0 and a real and field-independent parameters if ψ_1 and ψ_2 are real functions. This is the case when the molecule orbits involved in hopping are localized or not degenerated[13]. In this case, $P \propto |t|^2 = a(B^2 + B_0^2)$ and the polaron density shall depend on the magnetic field as $\frac{P}{\gamma(P_0+P)}J + n_0 = n_0' + \alpha B^2/(B^2 + B_0^2)$, where n_0, n_0', α and B_0 are B-independent parameters that depend on the molecule orbits involved. Thus, $B^2/(B^2 + B_0^2)$ is a natural OMFE function for $t = B_0 + iaB$. The second type of empirical function appears naturally for $t = i(B_0 + aB)$. According to Eq. (2), this can happen when the spatial derivatives of ψ_1 or ψ_2 are the functions multiplied by pure imaginary numbers. Of course, this must correspond to degenerated states. In this case, the leading term in the polaron density takes a form of $[B/(B+B_0)]^2$ in a similar argument when $P \gg P_0$. In reality, electron (polaron) hopping between two organic molecules should involve many molecule orbits, especially in photophysical processes and in a high electric field. One then needs to add contributions from all hopping events. Thus, it is likely that both $B^2/(B^2 + B_0^2)$ and $[B/(B + B_0)]^2$ processes are presented, and OMFE should then be fitted by the linear combinations of these two functions, consistent with experimental findings.

The novel mechanism is very robust. At the room temperature, the transport of charge carriers will involve many different molecule orbits. Each hopping event will subject to the influence of this mechanism as long as magnetic confinement is negligible ($l_B > d$) and molecular structure is not sphere-like. Of course, thermal average over all hopping events is needed. Molecule-molecule orientation in organic semiconductors should be quasi-random due to the nature of organic molecules. A magnetic field can be along any direction with respect to the molecule-molecule bond instead of perpendicular direction as assumed in the above discussion. This explains why OMFE is not sensitive to the field direction in devices. According to Eq. (2), different angle between the field and molecule-molecule bond leads to different hopping coefficient. It should also be emphasized that the mechanism present here does not depend on electron spins, and it does not require large energy splits of different spin configurations. It is applicable to both bipolar and hole-only (or electron-only) devices. Differ from the previous theories that try to relate the OMFE to the changes of electron levels, the present theory attributes the OMFE to the change of electron hopping coefficient in a field. Thus, it does not have all the troubles as those spin-dynamics related theories involve concepts of excitons and bipolarons [6–10].

In conclusion, we present a novel mechanism for the OMFE for nonmagnetic organic semiconductors. The mechanism is very general and robust for organic semiconductors, but is normally not important for usual covalently bonded inorganic semiconductors. The mechanism can not only explain all experimentally observed OMFE, but also provides a solid theoretical basis for the empirical OMFE formulas. New experiments are needed to firmly establish this mechanism as the genuine cause of the OMFE.

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